

Claims:

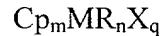
The following is claimed:

1. A metallocene supported catalyst composition comprising:
5 a metallocene catalyst; and
a support composition represented by a formula

Sup F

wherein Sup is a support and F is a fluorine atom bound to the support.

10 2. The metallocene supported catalyst composition of claim 1 wherein the metallocene catalyst is represented by a formula:



15 wherein Cp is a cyclopentadienyl ring which may be substituted, or derivative thereof which may be substituted, M is a Group 4, 5, or 6 transition metal, R is a hydrocarbyl group or hydrocarboxy group having from one to 20 carbon atoms, X may be a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group and m=1-3, n=0-3, q=0-3, and the sum of m+n+q is equal to the oxidation state of the transition metal.

20 3. A metallocene supported catalyst composition comprising:
a metallocene catalyst; and
a support composition represented by a formula

Sup L F_n

25 wherein Sup is a support selected from the group consisting of talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride or substituted polystyrene;

30 "L" is a first member selected from the group consisting of (i) bonding, sufficient to bound the F to the Sup; (ii) B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr bound to the Sup and to the F; or (iii) O bound to the Sup and bound to a second member selected from the group consisting of B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr which is bound to the F;

"F" is a fluorine atom; and

"n" is a number from 1-7.

4. The metallocene supported catalyst composition of claim 3 wherein the support composition is a fluorided support composition.

5. The metallocene supported catalyst composition of claim 3 wherein the metallocene catalyst is represented by a formula:



10 wherein Cp is a cyclopentadienyl ring which may be substituted, or derivative thereof which may be substituted, M is a Group 4, 5, or 6 transition metal, R is a hydrocarbyl group or hydrocarboxy group having from one to 20 carbon atoms, X may be a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group, and m=1-3, n=0-3, q=0-3, and the sum of m+n+q is equal to the 15 oxidation state of the transition metal.

6. The metallocene supported catalyst composition of claim 3 further including an activator.

20 7. The metallocene supported catalyst composition of claim 6 wherein the activator is an alkylalumoxane.

8. The metallocene supported catalyst composition of claim 6 wherein the activator is a noncoordinating anion activator.

25 9. The metallocene supported catalyst composition of claim 3 wherein the metallocene is selected from the group consisting of: Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl)Zirconium dimethyl

Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl) Zirconium dimethyl;

30 Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl) Zirconium dimethyl;

Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl) Zirconium dimethyl;

Dimethylsilandiylbis (2-ethyl-4-naphthyl-1-indenyl) Zirconium dimethyl,

Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2-methyl-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl) Zirconium dimethyl,
5 Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2-methyl-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2-ethyl-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl) Zirconium dimethyl,
Dimethylsilandiylbis (2-methyl-4-phenyl-1-indenyl) Zirconium dichloride
10 Dimethylsilandiylbis(2-methyl-4,5-benzoindenyl) Zirconium dichloride;
Dimethylsilandiylbis(2-methyl-4,6-diisopropylindenyl) Zirconium dichloride;
Dimethylsilandiylbis(2-ethyl-4-phenyl-1-indenyl) Zirconium dichloride;
Dimethylsilandiylbis (2-ethyl-4-naphthyl-1-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2-methyl-4-(1-naphthyl)-1-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2-methyl-4-(2-naphthyl)-1-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2-methyl-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2-methyl-4,5-diisopropyl-1-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2,4,6-trimethyl-1-indenyl) Zirconium dichloride,
Dimethylsilandiylbis(2-methyl-1-indenyl) Zirconium dichloride,
20 Dimethylsilandiylbis(2-ethyl-1-indenyl) Zirconium dichloride, or
Dimethylsilandiylbis(2,5,6-trimethyl-1-indenyl) Zirconium dichloride.

10. The metallocene supported catalyst composition of claim 3 wherein the
fluorine concentration is in the range of from 0.01 to 10.0 millimoles of fluorine
25 per gram of support.

11. A method of making a metallocene supported catalyst composition
comprising the step of:

30 contacting a metallocene catalyst with a support composition under suitable
conditions and for a sufficient time, wherein the support composition is
represented by a formula

Sup L F_n

wherein Sup is a support selected from the group consisting of talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride and substituted polystyrene;

"L" is a first member selected from the group consisting of (i) bonding, sufficient to bound the F to the Sup; (ii) B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr bound to the Sup and to the F; or (iii) O bound to the Sup and bound to a second member selected from the group consisting of B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr which is bound to the F;

"F" is a fluorine atom; and

"n" is a number from 1-7.

12. The method of claim 11 comprising the step of contacting the metallocene catalyst with an activator before contacting the metallocene with the support composition.

13. The method of claim 11 wherein the support composition is a fluorided support composition.

14. A polymerization method comprising the step of:

contacting a polymerizable olefin with a metallocene supported catalyst composition under suitable conditions and for a sufficient time wherein the metallocene supported catalyst composition comprises

a metallocene catalyst;

a support composition represented by a formula

Sup L F_n

wherein Sup is a support selected from the group consisting of talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride and substituted polystyrene;

"L" is a first member selected from the group consisting of (i) bonding, sufficient to bound the F to the Sup; (ii) B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re,

or Zr bound to the Sup and to the F; or (iii) O bound to the Sup and bound to a second member selected from the group consisting of B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr which is bound to the F;

"F" is a fluorine atom; and

5 "n" is a number from 1-7.

15. The method of claim 14 wherein the polymerizable olefin is propylene.

10 16. An article incorporating a polymer product of claim 14.

17. The article of claim 16 comprising a member selected from the group consisting of films, fibers, fabrics, and molded structures.

15 18. The method of claim 14 wherein the support composition is a fluorided support composition.

19. A metallocene supported catalyst composition consisting essentially of:
one or more metallocene catalyst;
activator; and
a support composition represented by a formula

20 Sup L F_n

wherein Sup is a support selected from the group consisting of talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide thoria, aluminum phosphate gel, polyvinylchloride or substituted polystyrene and mixtures thereof;

25 "L" is a first member selected from the group consisting of (i) bonding, sufficient to bound the F to the Sup; (ii) B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr bound to the Sup and to the F; or (iii) O bound to the Sup and bound to a second member selected from the group consisting of B, Ta, Nb, Ge, Ga, Sn, Si, P, Ti, Mo, Re, or Zr which is bound to the F;

30 "F" is a fluorine atom; and

"n" is a number from 1-7.

20. The metallocene supported catalyst composition of claim 19 wherein the support composition is a fluorided support composition.

21. The metallocene supported catalyst composition of claim 19 wherein the metallocene catalyst is represented by a formula:



wherein Cp is a cyclopentadienyl ring which may be substituted, or derivative thereof which may be substituted, M is a Group 4, 5, or 6 transition metal, R is a hydrocarbyl group or hydrocarboxy group having from one to 20 carbon atoms, X may be a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group, and m=1-3, n=0-3, q=0-3, and the sum of m+n+q is equal to the oxidation state of the transition metal.

22. The metallocene supported catalyst composition of claim 19 wherein the fluorine concentration is in the range of from 0.6 to 3.5 wt. % of support.